

# **Frame-Transfer Gating (FTG) Raman Spectroscopy for Time-Resolved Multiscalar Combustion Diagnostics**

by

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## **Brief Abstract**

We disclose a novel spontaneous Raman scattering detection technology, which utilizes a frame-transfer charge-coupled-device (CCD) sensor, in conjunction with a pulsed laser and multiplex optical fiber collection, to realize time-resolved Raman spectroscopy of turbulent flames that is free from optical background noise (interference). This invention is a significant advancement that redefines the experimental approach to multiscale diagnostics in combustion. The technology permits not only shorter temporal optical gating (down to  $<1\ \mu\text{s}$ , in principle) but also higher optical throughput, thus resulting in a substantial increase in measurement signal-to-noise ratio.

## **I. Description of Problem and Prior Art**

### *General description of problem:*

Accurate experimental measurement of spatially and temporally resolved variations in chemical composition (species concentrations) and temperature in turbulent flames is vital for characterizing the complex phenomena occurring in most practical combustion systems, such as gas turbine engines, power utility boilers, and internal combustion engines. These diagnostic measurements are called multi-scalar because they are capable of acquiring multiple scalar quantities simultaneously. Multiscale diagnostics also play a critical role in the area of computational code validation. In order to improve the design of combustion devices, computational codes for modeling turbulent combustion are often used to speed up and optimize the development process. The experimental validation of these codes is a critical step in accepting their predictions for engine performance in the absence of cost-prohibitive testing. The present invention addresses this need by significantly improving the quality and ease of collection of Raman data, through the use of a novel detection architecture with remarkable noise removal capabilities.

### *Key problem characteristics:*

Non-intrusive laser diagnostics play a major role in combustion characterization and code validation. In particular, spontaneous Raman scattering (inelastic light scattering from rotating and vibrating molecules) has been a popular method of probing flames because it is practically the only technique that provides spatially and temporally resolved multiscale measurements. Although spontaneous Raman scattering (SRS) spectroscopy is routinely used for combustion

diagnostics [Barlow, 2007], accurate determination of flame characteristics from SRS remains a challenge due to inherently weak signals.

One of the most critical aspects of setting up a time-resolved SRS diagnostic system is the temporal optical gating scheme. A short optical gate is necessary in order for weak SRS signals to be detected with a good signal-to-noise ratio (SNR) in the presence of strong background optical emissions. This time-synchronized optical gating is classical problem even to other spectroscopic techniques such as laser induced fluorescence (LIF) or laser-induced breakdown spectroscopy (LIBS). Traditionally, experimenters have had basically two options for gating: (1) an electronic means of gating using an image intensifier (II) before the CCD; or (2) a mechanical optical shutter (a rotary chopper /mechanical shutter combination).

Many groups have chosen the II for Raman diagnostics due to its nanosecond gating capability. However, the use of an II for Raman diagnostics often means a compromise in data quality. Due to photon spread from proximity focusing in the internal fiber-optic coupling plate between the II and the CCD array, the spatial resolution of the CCD array (and thus spectroscopic resolution) is compromised. In addition, due to avalanche gain and space-charge effects, the dynamic range of an II is limited to about 1000:1 (about 10 bits) for most practical applications. This relatively low dynamic range (or output saturation limit) can be problematic in cases where large differences exist in signal intensity of one species to another (e.g., a hydrocarbon vs. CO<sub>2</sub> in fuel rich flames). Finally, it has also been reported that II-CCD's can be vulnerable to bright laser sparks or other inadvertent bright sources of light and possibly damaged.

Alternatively, a high-speed mechanical shutter system is an excellent gating method that provides microsecond optical gating (see **Fig. 1a**). The combination of digitally-synchronized high- and low-frequency rotary optical choppers (custom 2- and 60-slot wheels) with a fast electro-mechanical leaf shutter can provide a 10  $\mu$ s gate at typical repetition rates required for pulsed-laser measurements (10-30 Hz) [Nguyen, 2005]. With the shutter system, one can take full advantage of the high dynamic range ( $10^5 / e^-$  typical) and high quantum efficiency (QE) (> 90% typically) offered by a conventional cooled back-illuminated CCD (BI-CCD). On the other hand, the use of a shutter results in a transmission loss of about 50%, due to internal coupling and chopping losses. The shutter system also has a certain amount of jitter, which requires additional optics for monitoring and correction. In addition, an electro-mechanical leaf-shutter

has a relatively short life-time (1-2 years) under typical usage cycles in diagnostic experiments.

Regardless of the type of gating employed, laser-generated optical background (e.g., laser-induced fluorescence from polycyclic aromatic hydrocarbons, PAH or C<sub>2</sub> carbon) may still be a problem since such phenomena occur simultaneously with Raman scattering (within the nanosecond time window). To combat this issue, “interference-free” Raman techniques have been proposed [Grünefeld, 1995]. The basic concept (which will be applied to the current invention in a different system architecture) involves isolating the highly polarized Raman scattering signal from the unpolarized laser-induced fluorescence. An attempt was made to apply this principle in isolating the Raman signal from the optical background on a single-shot basis using II-CCD cameras with a polarizing beamsplitter [Cléon, 2006]. This attempt was not successful, however, because of reduced optical throughput (typically >50% loss at polarizer) and insufficient spectral data quality due to the use of an II.

## **II. Technical Description of the Concept of the Technology**

### Overview: Concept

The new technology presently disclosed is an experimental method (or scheme) for isolating true Raman spectral signals from flames using a single CCD detector. The technology does not use an image intensifier or a mechanical shutter. Individual electrical or optical devices employed in this method are NOT new technology. However, the diagnostic methodology itself, which utilizes a combination of existing devices for a particular application, *is* a novel concept, as explained below.

The present methodology, which is a new paradigm for conducting time-resolved Raman spectroscopy, employs two key optical devices: a pulsed laser (nanosecond pulses) and a frame-transfer CCD sensor. Frame-transfer CCD sensors have been historically used to capture fast (microsecond time scale) transient events, such as Bose-Einstein Condensate phenomena, over a short period of time (milliseconds). By their operation, the sensor area is exposed for a certain time and the charge is then transferred to the frame transfer area (or masking area) row by row and is read out via a gain register or serial register. This is called 'frame-transfer' readout or 'kinetics' readout. The idea of using frame-transfer readout for gating out flame background emissions in Raman spectroscopy has never been discussed. Moreover, the use of frame-transfer readout provides a very effective way of isolating true Raman signal from laser-generated optical

interferences in any combustion environment in principle without an employment of multiple CCD detectors or polarizer on detection side.

### Technical Description

#### *1. Frame-Transfer Gating (FTG) Raman Spectroscopy*

**Fig. 1b** shows an example of Raman spectroscopy in flames with a frame-transfer CCD sensor and a pulsed laser. In this example, a nanosecond (10-100 ns) long laser pulse excites major species molecules (such as N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, etc.) in flames. Raman scattering from these molecules is collected by a lens assembly and focused onto an optical fiber (a single fiber or fiber bundle arranged in a packed round or alternative geometry), which guides the scattered light to the entrance slit of a spectrograph. Unlike a mechanical shutter-based system (**Fig. 1a**), there is no optical transmission loss associated with this gating system. The scattering can also be directly focused onto the slit entrance of the spectrograph if such an arrangement is preferred.

**Fig. 2** shows how a true Raman spectrum can be obtained by the frame-transfer readout. As shown in **Fig. 2** (upper left), the CCD sensor is only partially illuminated; the incident illumination is limited by an optical fiber (which is the case in **Fig. 1b**) or by masking at the entrance to the spectrograph. In the frame-transfer readout mode, the sensor continues to shift each row toward the masking area (physically masked and thus no light sensitivity) until this electron charge "storage" area is full. During this period, an excitation laser pulse interrogates a flame of interest, initiating Raman scattering. Since the unmasked CCD pixels (silicon) are always light sensitive, this Raman scattering is captured within the illuminated area in the form of a spectrum. While this series of events — laser excitation, scattering, photo-sensing, and electron-discharge — takes place within a time period of roughly 100 nanoseconds, shifting of the resulting electrons generated within the illuminated area ( $n$  rows) takes relatively longer time, typically microseconds. For a state-of-the-art frame-transfer CCD device<sup>2</sup>, the vertical shift rate can be as fast as 300 ns/row (for a 512 x 512 pixels CCD sensor). If an optical fiber with a 100  $\mu\text{m}$  core is the input to a 1:1 imaging spectrograph and the pixel size of the CCD sensor is 16  $\mu\text{m}$ /pixel, the illuminated area is approximately 7 pixels high. Thus, in this example, the frame-transfer rate can be as fast as  $300 \text{ ns} \times 7 \text{ rows} = 2.1 \text{ } \mu\text{s}$  per sub-frame (illuminated area). This

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[http://www.princetoninstruments.com/Uploads/Princeton/Documents/Datasheets/Princeton\\_Instruments\\_ProEM\\_%20512B\\_revM2.pdf](http://www.princetoninstruments.com/Uploads/Princeton/Documents/Datasheets/Princeton_Instruments_ProEM_%20512B_revM2.pdf)

means any sub-frame would be shifted out of the illuminated area to the non-illuminated area in 2.1  $\mu\text{s}$ . Here it is important to understand that the illuminated area of the sensor constantly receives light from the flame. In the absence of a laser pulse, this background flame emission is essentially blackbody (and flame chemiluminescence spectral emission) radiation from the probe volume. CCD pixels exposed to this background flame emission accumulates additional electron charges. Once the sub-frame with the Raman spectral information is shifted out of the illuminated area, there will be no optical noise that can interfere with the signal (there will be noise due to dark current, but this is significantly less than the signal counts). At this point, the background flame emission is "shut out." Therefore, *the frame-transfer rate essentially defines the 'gate width' of the Raman scattering measurement*. It should be noted that a trade-off relationship exists between the gate width (frame-transfer rate) and signal level. As the fiber core diameter (or size of the fiber array at the entrance slit) is increased, the signal level increases, but the size of the illuminated area also increases (there is a greater number of rows). This results in a slower frame-transfer rate and, consequently, a longer gate width. Consequently, the size of the sub-frame will need to be optimized for each unique flame condition and diagnostic configuration (laser power, collection solid angle, and f/number of spectrograph).

In addition, supplemental physical masks can be integrated to a camera system above a certain region in the CCD sensor array to serve as a light-blocking shield for the image storage areas. This would further limit stray light within the spectrograph. The same outcome can be achievable by adjusting the positioning of the CDD chip so that the fiber image lies exactly at the bottom edge of the built-in physical mask already provided by the frame-transfer CCD.

An example of the timing control scheme for frame-transfer gating (FTG) Raman spectroscopy is shown in **Fig. 3**. In this example, the first delay generator (master control) triggers the frame-transfer CCD sensor to stop the so-called continuous cleaning<sup>3</sup>, which almost instantly<sup>4</sup> activates the exposure of the CCD sensor (i.e., the accumulation of electron charges). Immediately after a pre-determined exposure time, each sub-frame is shifted out of the illuminated area over a time period defined by the frame-transfer rate and the exposure of the

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<sup>3</sup> It constantly shifts electron charges from the sensor area into the masking area. This keeps the CCD sensor "free" from dark current noise until a trigger comes for a measurement. As a result, the sensor can be considered to be normally "closed" just like a mechanical shutter.

<sup>4</sup> There is up to a few microseconds of jitter between a stop of the continuous clean and the actual start of frame shifting. However, this jitter can be easily overcome by having an additional "exposure-start" signal from the sensor.

next sub-frame begins. In FTG-Raman spectroscopy, the exposure time  $c$  should be set to zero ( $= 0$ )<sup>5</sup> in order to achieve the shortest gate width. Therefore, the sensor timing diagram becomes essentially just a series of frame shifting cycles without any exposures. The same generator triggers (either directly or via a second delay generator) the laser<sup>6</sup> flash lamp followed by the Q-switch trigger for full-energy laser pulse emission (10 nanoseconds) after the typical Q-switch delay (ca. 200 microseconds).

FTG-Raman spectroscopy was demonstrated using a stoichiometric methane-air flame (see **Fig. 4**). It is clearly seen that the quality of the Raman spectrum measured with the frame-transfer gating method surpasses the equivalent measurement with a conventional mechanical shutter system. Notice in particular that the inherently weak Raman scattering from carbon dioxide (CO<sub>2</sub>) is easily observed by FTG-Raman spectroscopy. This increase in signal-to-noise ratio is mainly due to the high optical throughput that was achieved. This result clearly shows the promise of FTG-Raman spectroscopy for combustion diagnostics.

## *2. Method of Flame Background Correction in FTG-Raman Spectroscopy*

Even with the sub-microsecond gating realized by the FTG-Raman technology, the illuminated area of the sensor can collect (accumulate) a considerable amount of background flame emission depending on its magnitude. This background flame emission can be effectively corrected on shot-by-shot basis by subtraction in post-processing as illustrated in **Fig. 2**. Since each sub-frame collects background flame emission over the same duration of time (gate width), any sub-frame except the one with the Raman signal should provide a spectrum of the flame emission that is appropriate for background correction. The spectrum of flame emission, in general, does not dramatically change over time because it is a spatially integrated (line-of-sight) measurement, unlike laser scattering from a localized probe volume. However, it is best to use the sub-frame just next (before or after) to the Raman signal sub-frame, minimizing the time separation ( $<$ frame-transfer rate) between the signal sub-frame and the background sub-frame.

## *3. Method of Correction of Laser-Generated Optical Background in FTG-Raman Spectroscopy*

Another new technique can also be realized by extending the FTG-Raman technology to polarization-resolved diagnostics. No matter how short the gate width, laser-generated

<sup>5</sup> Note that regardless of the exposure time the sensor ALWAYS senses light and converts photons into electrons.

<sup>6</sup> A Nd:YAG Q-switched pulsed laser is typically used for visible Raman diagnostics in flames, although any pulsed laser can be used in this technology.

background emissions, such as laser-induced fluorescence (LIF) of  $C_2$  carbons or PAH, cannot be avoided since these emissions occur simultaneously with Raman scattering on a nanosecond time scale. This problem is universal to any Raman spectroscopy system for flame diagnostics, even those systems employing nanosecond-gate II-CCDs. The only solution to this problem is a polarization-resolved measurement. Since laser-induced background emissions are unpolarized, unlike Raman scattering which is polarized, they can be selectively isolated (and subtracted). While the theory of this polarization technique has been proposed previously [Grünefeld, 1995], the implementation of this technique for time-resolved Raman diagnostics has not been matured [Cléon, 2006]. A principal reason is that an enabling technology that can increase the signal-to-noise ratio was needed. **Figure 4** shows our proposed system, named polarization-resolved FTG-Raman spectroscopy. When a flame receives two orthogonally polarized, but otherwise identical, laser pulses, Raman scattering can be observable only for the vertically-polarized excitation pulse<sup>7</sup> at the orientation described in **Fig. 4**. The (unpolarized) laser-generated background emissions are observed regardless of the polarization state of the excitation pulses. If the two orthogonally-polarized laser pulses are *separated in time* so that they just fall onto a pair of consecutive sub-frames on the CCD sensor, subtracting the one (laser-generated background emission only) from the other (Raman signal plus background emission) results in a true Raman spectrum (see **Fig. 5**)<sup>8</sup>.

### III. Uniqueness and Novel Features

This invention could potentially benefit the development of advanced combustion engines for Aerospace, Defense, and civilian systems through either direct diagnosis of the systems or validating computational codes.

Uniqueness and novel features of the described technology include:

- + Fast electronic gating for spectroscopy.
  - Sub-microseconds ( $\sim 2 \mu s$ ) gate achievable.
  - No mechanical moving parts required.

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<sup>7</sup> Raman scattering is maximum in the plane orthogonal to a polarization direction of the excitation laser (and zero in the direction parallel to the incident polarization).

<sup>8</sup> Strictly speaking, the spectra contained in the pair of sub-frames are not simultaneously observed but semi-instant events. However, within the time of a typical frame transfer ( $\sim 10 \mu s$ ) discussed in this disclosure, flow in a combustion system can be considered to be "frozen" in space.



- Durable (as long as sensor lasts).
  - Simple but precise timing control.
  - Highly reproducible.
  - No timing jitter.
  - No need for an expensive, fragile image intensifier for gating. This enables the use of high-resolution back-illuminated CCD sensor without sacrificing image quality or spectral resolution
  - Higher signal-to-noise ratio (factor of ~5) due to higher optical throughput and potential shorter gate width
- + Enables time-, space-, and polarization-resolved Raman spectroscopy with single sensor and single collection optics, but without optical loss in the detection train (quantum efficiency > 90%)!
  - + Enables *real-time* optical background corrections (flame emission and laser-generated light emission/fluorescence).
  - + Enables *true* Raman signal measurements for more accurate combustion diagnostics (multiscalar information: temperature and chemical gas composition).
  - + Enables compact Raman detection system design.
  - + Beneficial for other spectroscopy and imaging such as laser induced fluorescence (LIF) or laser-induced breakdown spectroscopy (LIBS).

#### **IV. Speculation of Commercial Potential**

CCD sensor developers and manufacturers (i.e., Princeton Instruments).

#### **References**

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Grünefeld, G., Beushausen, V., Andresen, P., “Interference-free UV-laser-induced Raman and Rayleigh measurements in hydrocarbon combustion using polarization properties,” *Applied Physics B: Lasers and Optics* 61 (5), 473-478 (1995).

Nguyen, Q.-V., “High-speed electromechanical shutter for imaging spectrographs,” US Patent 6,937,331 (Aug. 2005).

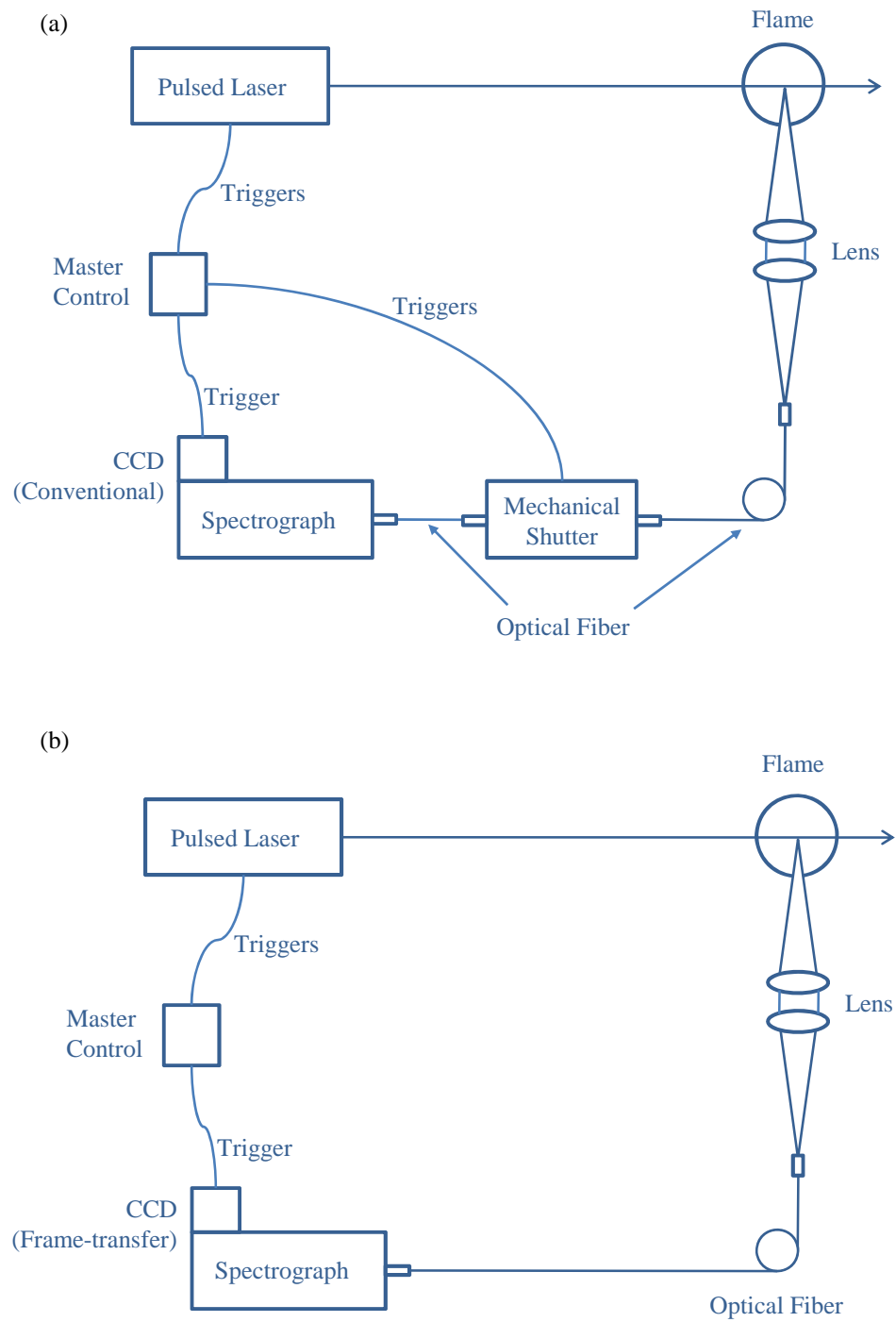


Fig. 1 Schematic of laser Raman spectroscopy apparatus. (a) Current state-of-the-art system with electro-mechanical shutter-based gating. (b) New system with a frame-transfer gating.

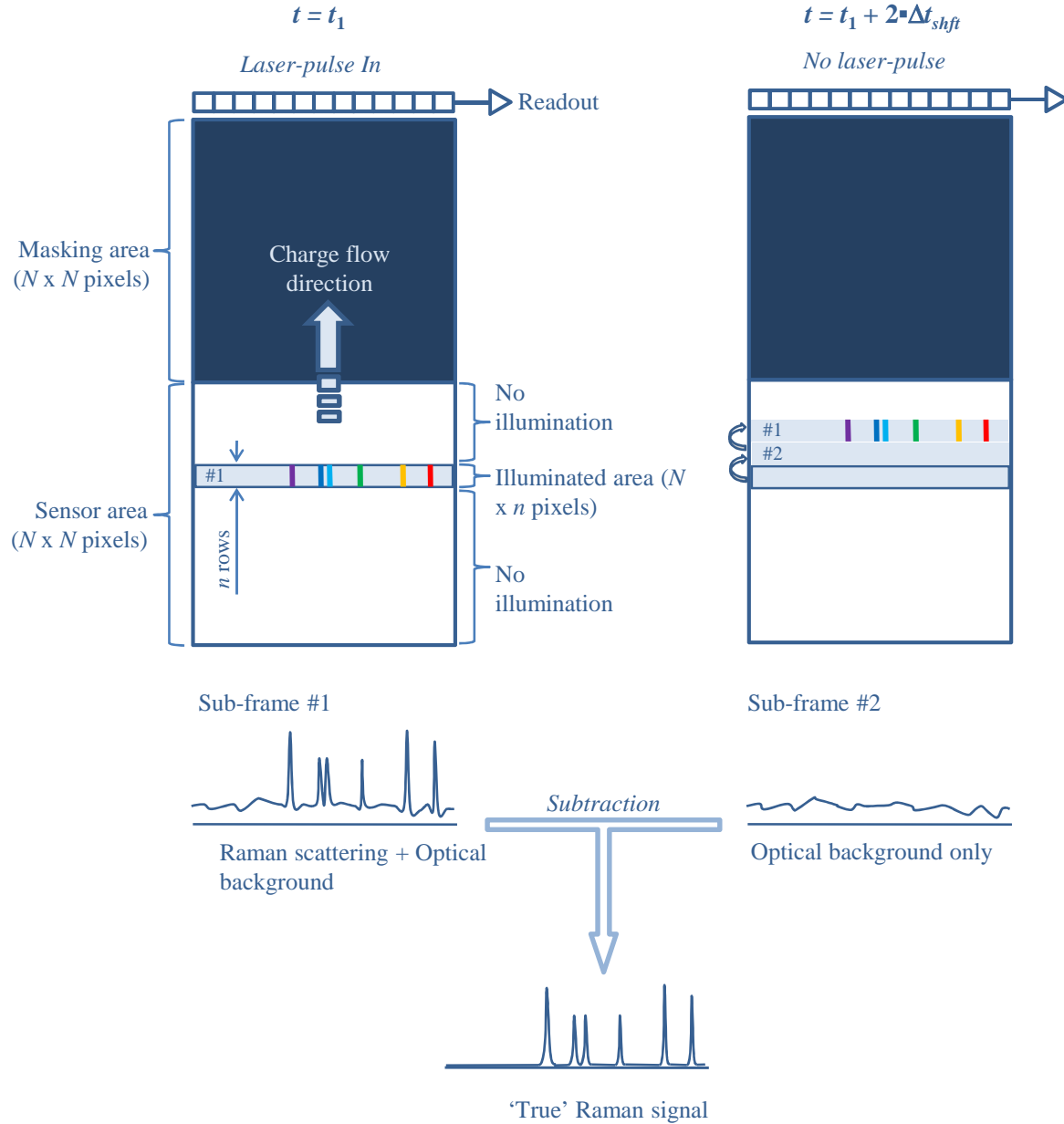


Fig. 2 True Raman signal acquisition architecture utilizing a frame-transfer CCD running in the so-called kinetics mode. The sensor area is partially illuminated (window size =  $n$  rows high). The optical fiber size defines the illuminated area, preventing light from falling on the rest of the sensor. In this diagram, Raman scattering excited by instant single laser pulse is captured in sub-frame #1, which is then shifted out of the illuminating area over a time  $\Delta t_{shift}$  ( $= n \times$  vertical shift time/row). This sub-frame shift time defines the temporal gating width, while the temporal resolution of Raman scattering is solely defined by the length of the laser pulse ( $\sim 10$  ns). Sub-frame #2 gets no laser pulse illumination (thus no Raman signal), but collects only optical background (i.e., flame luminescence) over the same period of time. A subtraction post-processing of these two sub-frame data sets produces a true Raman signal on a single-shot basis.

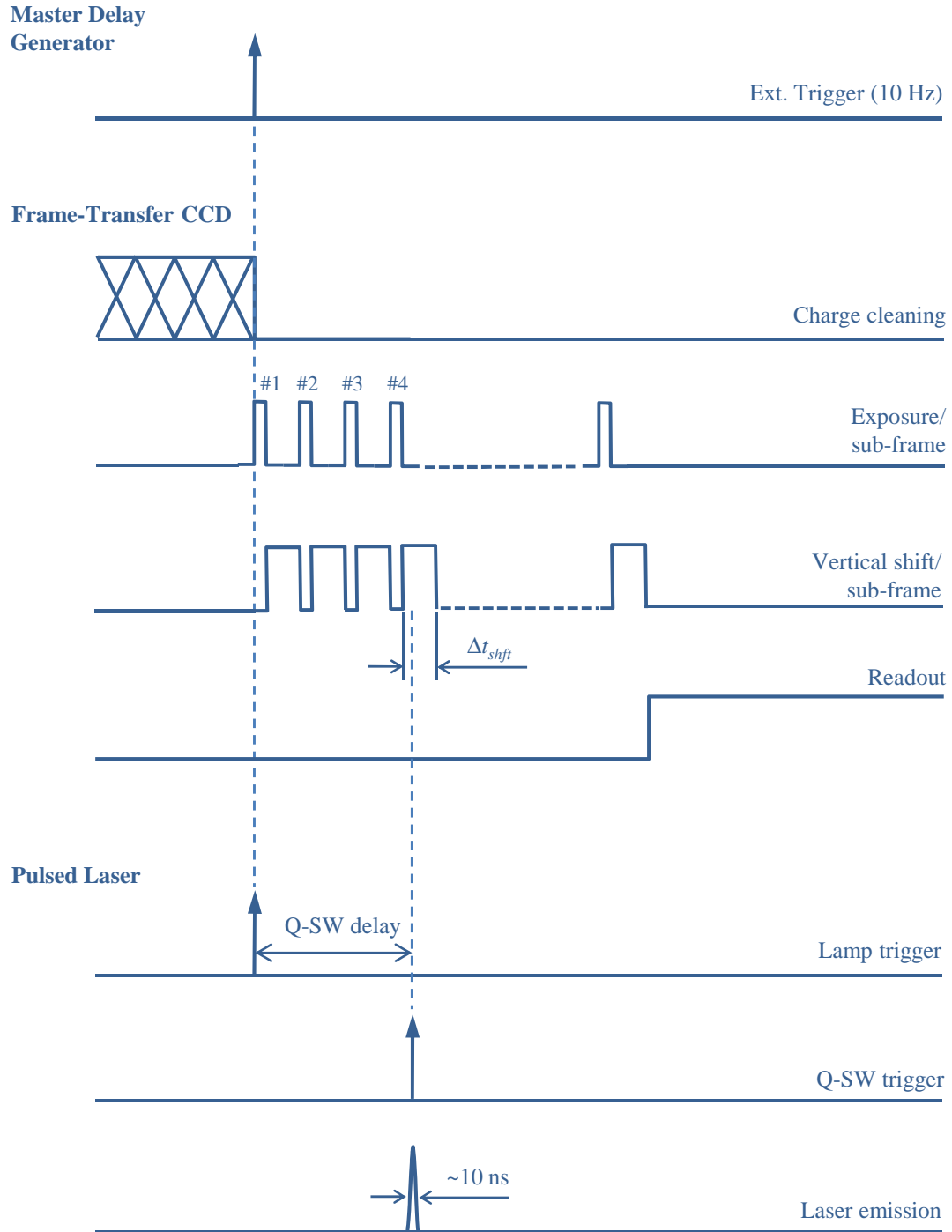


Fig. 3 Timing diagram for frame-transfer CCD detection applied to pulsed laser measurements. In this diagram, laser Raman scattering is captured in sub-frame #4. Exposure time can (should) be set to 0 to provide the shortest temporal resolution.  $\Delta t_{shift}$  (= gating width) is typically from 100's ns to 10's  $\mu$ s depending on the number of rows,  $n$ , of the sub-frame.

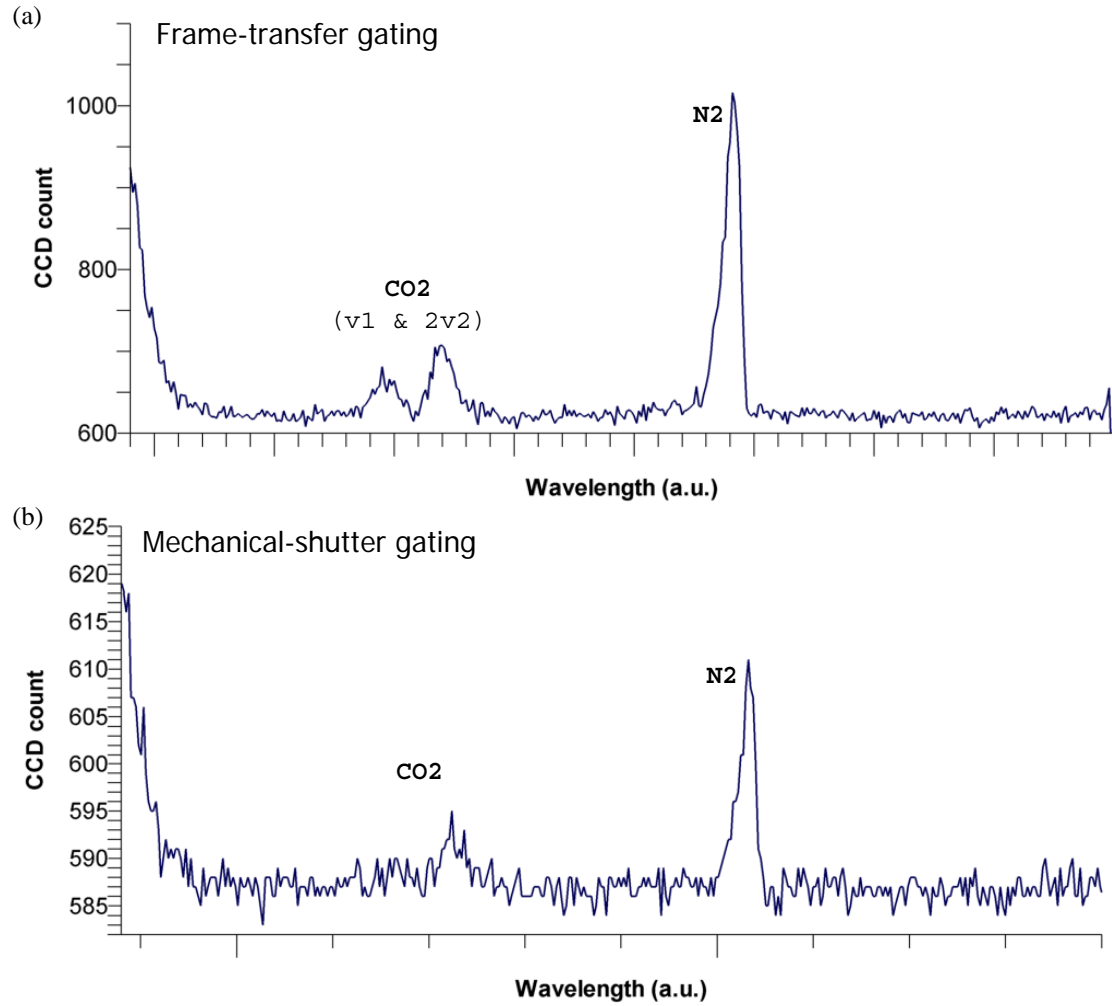


Fig. 4 Demonstration of single-shot detection of Stokes Raman spectra for a stoichiometric methane-air flame. (a) a frame-transfer back-illuminated CCD sensor with frame-transfer gating (see Fig. 1b). (b) a conventional back-illuminated CCD sensor with a mechanical shutter (see Fig. 1a). Laser pulse energy is 500 mJ/pulse. The plots only show a portion (from 540 nm to 640 nm) of the Raman spectra observable in flames. Gate width of both systems is 24  $\mu$ s in this test.

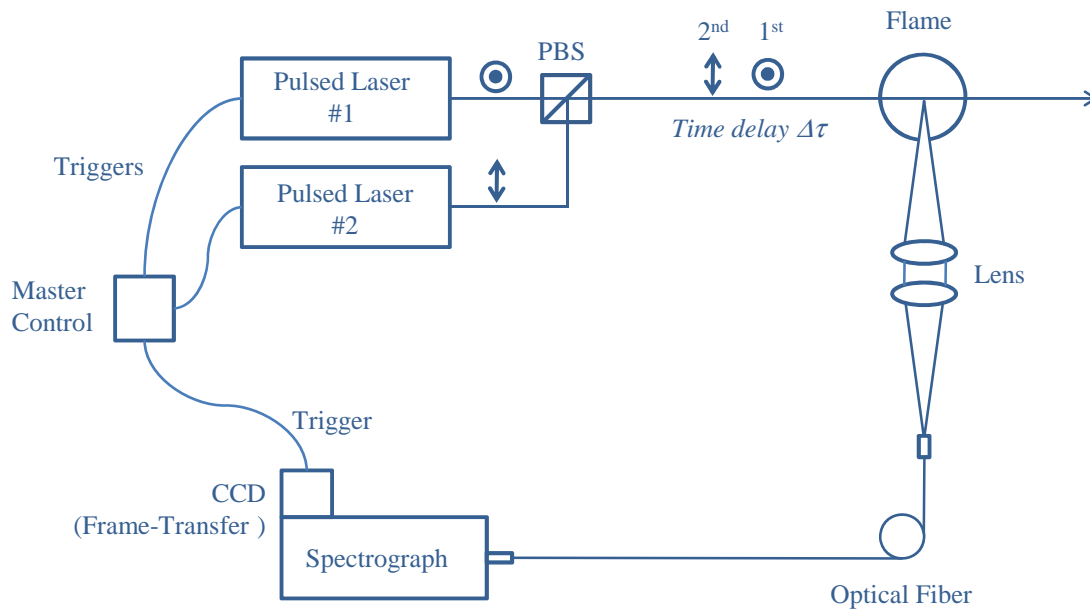


Fig. 5 Schematic of double-pulse polarization-resolved laser Raman spectroscopy apparatus. The time separation between the 1<sup>st</sup> and 2<sup>nd</sup> pulses,  $\Delta\tau$ , is equal to one sub-frame vertical shift time. PBS: polarization beam splitter. (Laser #1 & #2 polarizations should be switched relative to PBS operation – horiz passes thru and vert is reflection)

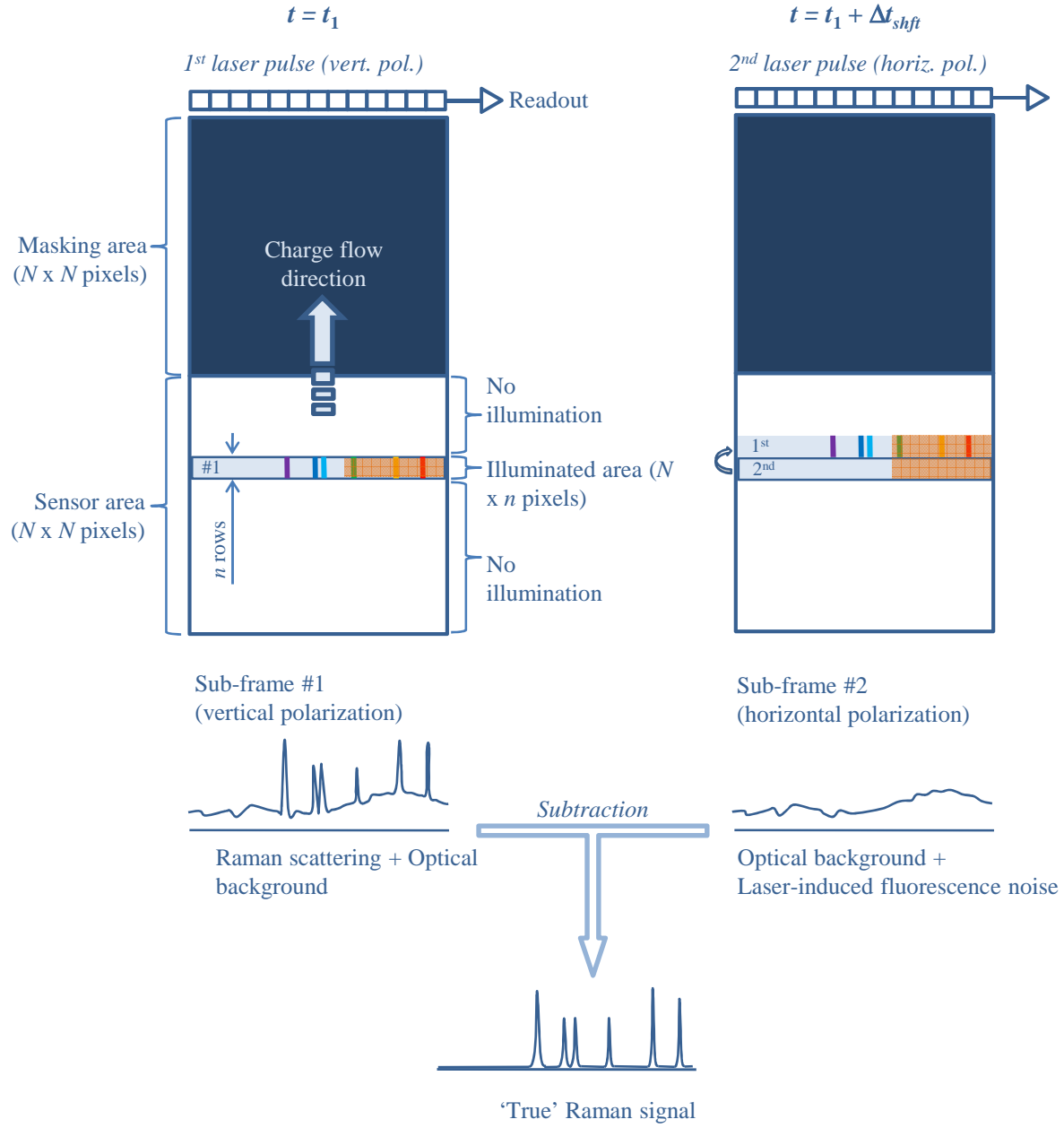


Fig. 6 Double-pulse polarization-resolved laser Raman spectroscopy architecture for interference-free Raman signal acquisition utilizing a frame-transfer CCD.